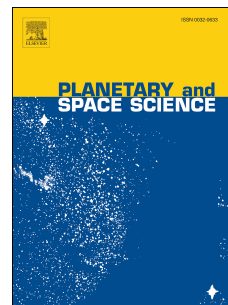


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Detecting aromatic compounds on planetary surfaces using ultraviolet time-resolved fluorescence spectroscopy

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Abstract

Many aromatic organic molecules exhibit strong and characteristic fluorescence when excited with ultraviolet radiation. As laser excitation in the ultraviolet generates both fluorescence and resonantly enhanced Raman scattering of aromatic vibrational modes, combined Raman and fluorescence instruments have been proposed to search for organic compounds on Mars. In this work the time-resolved fluorescence of a suite of 24 compounds composed of 2-5 ringed alternant, non-alternant, and heterocyclic PAHs was measured. Fluorescence instrumentation with similar specifications to a putative flight instrument was capable of observing the fluorescence decay of these compounds with a sub-ns resolution. Incorporating time-resolved capabilities was also found to increase the ability to discriminate between individual PAHs. Incorporating time-resolved fluorescence capabilities into an ultraviolet gated Raman system intended for a rover or lander can increase the ability to detect and characterize PAHs on planetary surfaces.

Keywords: Time-resolved fluorescence, ultraviolet, organics, astrobiology, polycyclic aromatic hydrocarbons

1. Introduction

The Mars 2020 rover, the successor to the Mars Science Laboratory (MSL), will further NASA's objective to seek signs of life and will have strong capabilities for the in-situ detection of biosignatures (Mustard et al. 2013). A primary objective of the mission is to determine if life existed on Mars by searching for biosignatures that may be preserved today. The Mars 2020 rover will include a 532 nm Raman system as part of the SuperCam instrument (Clegg et al. 2015), as well as a Deep-UV 248.6 nm Raman and fluorescence instrument (SHERLOC) (Beegle et al. 2015a). The SuperCam package contains instrumentation for imaging, mineralogical identification, and for determining elemental composition. Mineralogical capabilities are enabled by the Raman system, which contains an intensifier that provides 100 ns gating near the laser pulse, reducing fluorescence and ambient light, as well as permitting time-resolved fluorescence measurements as the gate is moved relative to the excitation pulse. The deep UV excitation of the SHERLOC instrument, which is attached to the rover arm, permits identification of potential biosignatures and organic material including aliphatic and aromatic compounds through measurements of pre-resonance and resonance Raman effects, as well as fluorescence in the UV region (Bhartia et al. 2008, Abbey et al. 2017). The putative instrument discussed in this work differs from both systems in that it incorporates an ultraviolet excitation as

well as an intensifier to enable time-resolved fluorescence measurements in the UV range, where many organic compounds exhibit fluorescence.

While the past and present habitability of Mars is uncertain, the recent analysis of reaction products from MSL's Sample Analysis at Mars (SAM) instrument indicate the presence of several aromatic compounds (Kerr 2014, Freissinet et al. 2015). Some of these compounds may have been generated from oxochlorines with organic material present in the rover (Glavin et al. 2013), however other compounds, including chlorobenzene, were detected at levels consistent with a Martian source of organic carbon (Freissinet et al. 2015). No positive detection of larger organics including PAHs has been reported, although laboratory calibration suggests that SAM may have difficulty detecting these classes of compounds (Millan et al. 2016). For future missions to Mars, icy worlds, and elsewhere in the solar system, instruments capable of locating organics that are both sensitive and require minimal sample processing can make important contributions to the identification of biotic and abiotic organic compounds. Raman and fluorescence spectroscopic instruments are sensitive to organic compounds, provide characteristic spectra, and can obtain measurements from stand-off distances with little or no sample preparation (Skulinova et al. 2014, Sharma et al. 2003). Organic compounds can generate both resonantly enhanced Raman scattering (e.g. Rava and Spiro (1985), Fodor et al. (1985), Asher et al. (1986), Dijkstra et al. (2001)) as well as strong fluorescence when excited with ultraviolet radiation (Tarcea et al. 2007), and therefore

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